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FLUORESCENCE DECAY OF THE 0, AND 1, STATES OF Xe2

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> > October, 1978

ABSTRACT

Synchrotron radiation from the Stanford storage ring (SPEAR) was used to measure the radiative decay constants of the lowestlying excited electronic states of Xe₂. Both a monochromator and interference filters were used in the fluorescence channel. The results suggest that at low pressures ($P_{Xe} < 125$ Torr) there is substantial deviation from the Stern-Volmer behavior predicted by the three-state models used previously to describe this lasing system. A new theoretical analysis was developed that includes participation in the kinetic scheme of intermediate vibrational levels of the 0_{11}^{+} and 1_{11} manifolds.

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I. INTRODUCTION

There has been a great deal of recent interest in the use of electronically excited systems as ultraviolet lasing media.¹ For the continued development of these lasers, a detailed knowledge of the dynamics of the lasing transitions is desirable. In particular, the lasing efficiency is dictated by the population inversion, which depends strongly on the lifetime of the upper level.

The lasing transition in Xe2, centered at 1700Å, involves radiative decay of both the (vibrationally relaxed) 0_{ij}^{+} and l_{ij} excited states to the 0_{α}^{+} ground state (see Fig. la).² Many attempts have been made to understand the salient dynamic processes of this system by the use of electron, $^{2-8}$ alpha-particle, 9 and optical¹⁰⁻¹⁴ excitation at a number of sample pressures. The electron and alpha-particle excitation modes involve indirect excitation mechanisms; e.g., the formation of $Xe_2(0_1^+)$ via three-body collisions.² In the case of optical excitation the situation is rather confused since previous workers have used a variety of excitation energies. Most of the energies chosen would allow the formation of excited states in Xe, via creation of Xe(${}^{3}P_{1,2}$) atomic states, as well as by population of the 0_{u}^{+} and 1_u manifolds directly from the 0_{σ}^+ ground state. This complication may well vitiate the conclusions that have been made about the 0_u^+ and 1_u^- lifetimes, even though photon excitation should in principle yield the least ambiguous results. In fact, previous work on Xe, has led to the proposal of several decay

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mechanisms and has yielded a wide range of τ_1 and τ_0^+ values, summarized in Table I.

In an attempt to clarify the situation we have used pulsed monochromatized synchrotron radiation to populate the upper vibrational levels of the 0_u^+ and 1_u^- electronic states of Xe₂ directly from the $X0_q^+$ ground state. Direct population of the lower levels is not possible because of their negligible Franck-Condon overlap with the bound portion of the $X0^+_{\alpha}$ manifold. Three types of time-resolved experiments were employed. The first involved monitoring the monochromatized fluorescent decay from the upper (first continuum) and lower (second continuum) vibrational levels of the 0_u^+ and 1_u^- states. The second was concerned with the measurement of total fluorescent decay at various sample pressures. The same sample pressures were used in the third type of experiment with interference filters in the fluorescence channel, which were used to emphasize fluorescent decay from the upper, and the lower vibrational levels of Xe, $(0_{u}^{+}, 1_{u})$. Section II describes the apparatus and the measurements that were carried out. In Section III the results obtained in the monochromatized (IIIA), total (IIIB) and filtered (IIIC) fluorescence experiments are described and compared with calculations based on a simple kinetic model. The overall conclusions of this work are presented in Section IV.

II. EXPERIMENTAL

The characteristic synchrotron pulse structure at the Stanford Synchrotron Radiation Laboratory (SSRL) (0.4 ns width, 780 ns repetition period) was utilized as a time base for time-

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resolved spectroscopy.¹⁵ Monochromatized radiation (8.7Å FWHM) from the 8° branch line at SSRL was used for excitation.

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A schematic diagram of our apparatus is shown in Fig. 2. Monochromatized radiation enters a bakeable UHV chamber before passing through a LiF window into a gas cell. Fluorescent radiation can then be detected below the cell. To ensure that no significant amounts of impurities were present in the sample, absorption spectra were measured using an optical photomultiplier (PMT) placed along the beam axis. A sodium salicylate film on the adjacent pyrex window served as a scintillator.

The monochromator experiment employed a highly polished, Pt-coated quartz toroidal mirror¹⁶ to focus fluorescent radiation onto the entrance slit of a GCA/McPherson 218 monochromator (operated at 50Å band pass). Because of the very low counting rates (2s⁻¹) encountered in the monochromatized fluorescence measurements, it was impractical to collect decay data at more than one pressure using this apparatus. However, pressure dependence of the non-monochromatized, total fluorescence decay was measured. In addition, broad-band interference filters were used, chosen to emphasize the two fluorescence continua separately: $1325 \pm 92\text{Å}$, and $1710 \pm 110\text{\AA}$ (Acton Research Corporation). (The 1325Å filter was chosen because wings of transmission stressed the vibrationally unrelaxed levels.) In this arrangement both the filter and the PMT window could be placed within 1 cm of the interaction region,¹⁵ resulting in typical counting rates of 1500 s⁻¹. In all experiments an EMR 510G photomultiplier tube

was used to detect the fluorescence. This PMT has a uniform response over the wave-length range under study. Using Rayleigh (prompt) scattering the overall time resolution was found to be 1.6 ns (FWHM).

All studies were carried out at ambient temperature (294K). The sample pressure of the 99.995% pure xenon was 68 Torr in the monochromator experiment and 5, 11, 25, 65, and 125 Torr in the total fluorescence and filter experiments, as measured using a calibrated transducer (I.C. Transducers, Inc.). Under these conditions the partial pressure of Xe₂ varies about a mean of $\simeq 0.001$ % of the total pressure.

III. RESULTS AND DISCUSSION

A. Monochromatized Fluorescence

Absorption of monochromatized radiation by Van der Waals' molecules in the ground state yields the upper excime'r state(s). At the resolution used for this study (8.7Å FWHM in excitation) it is possible to irradiate selectively below, at, or above the dissociation energy of a given excimer state. However, resolution in the fluorescence spectrum of fine structure within a vibronic manifold is not possible. Others^{10,11} have found the fluorescence spectrum, recorded with resolution >20Å FWHM, to have two broad bands centered at <u>ca</u>. 1510Å and <u>ca</u>. 1700Å. These are termed the "first continuum" and "second continuum", respectively. They are thought to arise from transitions from the top and bottom of the 0_u^+ and 1_u manifolds (see Fig. 1a). We qualitatively reproduced these spectra, though our excitation

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wavelength was 1508Å and our fluorescent band pass was 50Å FWHM (see Fig. 1b). By exciting at 1508Å (>2kT below the ${}^{3}P_{2}-{}^{1}S_{0}$ atomic resonance at 1491Å), we were able to avoid much of the complexity associated with atomic metastable production 10 and extract the relevant lifetimes reported below. Figure 3 shows time-resolved fluorescent decay curves taken at fluorescence wavelengths that emphasize the two continua separately.

A pseudo-potential calculation by Ermler, Lee, and Pitzer¹⁸ predicts a change in $0_{\rm u}^+$ radiative lifetime from <u>ca</u>. 3 ns at the top of the manifold to <u>ca</u>. 5 ns at the bottom. The corresponding values for the $1_{\rm u}$ radiative lifetime are expect to be <u>ca</u>. 40 ns at the top, and <u>ca</u>. 160 ns at the bottom of the manifold. This variation in lifetimes arises for three reasons; firstly, a change in coupling from Hund's case (a) at short internuclear distance to case (c) coupling at large internuclear distance.^{18a} Secondly, spin-orbit coupling mixes a ${}^{1}\Pi_{\rm u}$ state into the $1_{\rm u}$ manifold at large values of internuclear distance, which serves to increase the $1_{\rm u}$ - $0_{\rm g}^+$ transition moment. The third reason for the variation in radiative lifetime with internuclear distance is the wellknown ν^{3} dependence of dipole transition probability.

Only a single, short-lived ($\tau = 2.1 \pm 0.1$ ns) component is observed at the first continuum wavelength of 1514 ± 25 Å (Fig. 3a). The calculations of Ermler, Lee, and Pitzer¹⁸ indicate that the 0⁺_u state will be preferentially populated on excitation (by a factor of 10 over 1_u production); hence it is likely that fluorescence at the first continuum arises mainly

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from the decay of the 0_u^+ state. Furthermore, at 68 Torr the decay of upper vibrational levels of both states is strongly influenced by collisional effects. Very short lifetimes (<1.6 ns, our instrumental response) are therefore expected for both states, and it is unlikely that the relatively weak 1_u first continuum component would be resolved in our experiment.

Fluorescence at the second continuum energy yields two decay components (Fig. 3b; the shorter component is depicted more clearly on an expanded time scale in Fig. 3c). We assign these two components to decay of the lowest vibrational levels of the 0^+_u manifold¹⁹ (6.9 ± 0.3 ns) and of the 1^-_u level (112 ± 2 ns), respectively, in approximate agreement with other workers.²

All but the lowest vibrational levels of the 0_u^+ and $1_u^$ manifolds can decay either radiatively or via collisions. The lifetime of either the 0_u^+ or 1_u^- state obtained at the first continuum is a composite of these two processes; i.e.,

 $\tau_1^{-1} = \tau_{r1}^{-1} + kP$

where τ_{rl} is the radiative lifetime of the upper levels, k is the rate constant for collisional decay and P is the Xe pressure.

The lowest vibrational levels of the 0_u^+ and 1_u manifolds are populated collisionally from upper levels. Hence, in the high-pressure limit the derived lifetimes approach the true high-pressure radiative lifetimes at the second continuum energy. The rate equations governing this system are just those of two

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radioactive decay series decaying independently in cascade (assuming no intersystem crossing), with only the first of each species initially present. This problem was solved analytically by Bateman.²⁰ While it is completely straightforward to apply the Bateman equation to a decay chain of any length, we shall for brevity consider the case of two consecutive decays for each manifold, to compare our 0^+_u and 1^-_u lifetimes with those of Bonfield, et al.²¹ The decay rate from the bottom of each electronic manifold, following a singlestep collisionally-induced deactivation mechanism from the top of the manifold, is given by

$$\frac{\mathrm{dN}_2}{\mathrm{dt}} = c \left[e^{-t/\tau} r^2 - e^{-(\tau r^{-1} + kP)t} \right]$$

where τ_{r2} is the lifetime in the second continuum; i.e., at the <u>bottom</u> of the manifold, τ_{r1} and kP are as defined above, and C is a constant. The fluorescence intensity from the second continuum, dN_2/dt , rises through a maximum then decreases with time with a behavior approaching exponential decay in the limit $t \neq \infty$. If we choose a reference time T well beyond the maximum intensity, and if the conditions $\tau_{r1}^{-1} + kP >> \tau_{r2}^{-1}$, $(\tau_{r1}^{-1} + kP)T >> 1$ are satisfied, then the characteristic time interval τ_2 over which dN_2/dt decreases by a factor of e will quite closely approximate the true decay time τ_{r2} . We may relate our measured value of τ_2 to τ_{r2} and $(\tau_{r1}^{-1} + kP)$ by the expression

$$e^{-T/\tau}r^{2} - e^{-(\tau_{r1}^{-1} + kP)T} = e\left[e^{-(T + \tau_{2})/\tau}r^{2} - e^{-(\tau_{r1}^{-1} + kP)(T + \tau_{2})}\right]$$
(1)

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Bonfield, et al.,²¹ working at $P_{Xe} \ge 500$ Torr, found, at the second continuum, lifetimes of 4.8 ns (0_u^+) and 100 ns (1_u) and a feeding rate, $(\tau_{r1}^{-1} + kP)$, of 0.179 ns⁻¹. Using Eq. (1) these values suggest measured lifetimes τ_2 at 68 Torr of <u>ca</u>. 8 ns (0_u^+) and 101 ns (1_u) . The remaining discrepancy between our results and theirs probably arises from several factors. For example, at 68 Torr a multi-level model is required to describe the decay kinetics, i.e., the two decay model is an oversimplification. In addition, the lifetime τ_{r2} may actually be pressure-dependent at high pressures, especially for the long (1_u) component.

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It is pertinent at this point to compare our results with those of Dutuit, et al., 14 who investigated the second continuum fluorescence of Xe, using the ACO storage ring. They also utilized a monochromator in the fluorescence channel, set at 1750 ± 20Å and 1730 ± 20Å. At their longest excitation wavelength (1493Å) they observed a two-component decay, with the first lifetime increasing from 6.0ns at 50 Torr to 10.8ns at 200 Torr and the second being ca. 500-700ns over the same pressure range. There is a large discrepancy between our respective results for the long component. The origin of this discrepancy probably resides in the short (73ns) repetition period of ACO, which in this case will give rise to a poorly determined background. Additionally, it could be due to the use of an excitation wavelength (1493Å) which is within 2kT of the Xe ${}^{3}P_{2}$ - Xe ${}^{1}S_{0}$ absorption line, though there is fair agreement with our results for the short component.

B. Total Fluorescence

In general, least-squares fitting of the total fluorescence data yielded a three-component exponential decay. The results of the data analysis are shown in Table II. The reciprocals of the long and intermediate lifetime components are plotted against pressure in Figs. 4 and 5. It is clear that they deviate from the Stern-Volmer type of behavior expected if the models used previously to describe the system were valid in this pressure regime.¹¹ Generally, these models have involved the radiative decay of the upper populated levels of the 0_u^+ and 1_u states (first continuum) as well as non-radiative decay to the lowest levels followed by radiative decay of these lower levels¹¹ (responsible for the second continuum). A more rigorous model is outlined below which allows for fluorescence from all vibrational levels in the 0_u^+ and 1_u manifolds, as well as for collisionally induced relaxation.

Excitation of Xe₂ at 1508Å will populate vibrational levels of the 0⁺_u and 1_u states near the top of their manifolds (see Fig. 1a). Following excitation, these levels can decay either radiatively (to the X0⁺_g ground state of Xe₂) or via collisions to lower vibrational levels. Intersystem crossing between the 0⁺_u and 1_u states is possible. However, Keto et al.¹⁷ found that the rate constants of intersystem crossing are small ($10^{-24} - 10^{-22}$ cm³ns⁻¹) and they were not included in our calculation.

The decay of each manifold was represented in our model ' by the following reactions:

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$$Xe_{2}(0_{g}^{+}) + h\nu - Xe_{2}^{i} v=50 \text{ (instantaneous)}$$

$$Xe_{2}^{i} v=50 - Xe_{2}(0_{g}^{+}) + h\nu$$

$$Xe + Xe_{2}^{i} v=50 - Xe + Xe_{2}^{i} v=49$$

$$Xe_{2}^{i} v=49 - Xe_{2}(0_{g}^{+}) + h\nu$$

$$Xe + Xe_{2}^{i} v=49 - Xe + Xe_{2}^{i} v=48$$

$$\vdots$$

$$Xe_{2}^{i} v=49 - Xe_{2}(0_{g}^{+}) + h\nu$$
(2)

The radiative decay constant of the 0_u^+ manifold was varied linearly with v from $k_{50} = 0.386 \text{lns}^{-1}$ to $k_0 = 0.1859 \text{ns}^{-1}$, the corresponding values for the 1_u state being 2.564 × 10^{-2}ns^{-1} and $6.212 \times 10^{-3} \text{ns}^{-1}$. These reciprocal radiative lifetimes were taken from the pseudo-potential calculations of Ermler, Lee, and Pitzer.¹⁸ They are values found at points on the 0_u^+ and 1_u potential curves, and Franck-Condon effects were not included in the calculation. The non-radiative decay constants were also varied linearly, from $k_{50}^{*} = 4.4 \times 10^{-18} \text{cm}^3 \text{ns}^{-1}$ to $k_1^{*} = 1.76 \times 10^{-19} \text{cm}^3 \text{ns}^{-1}$. These values were used for both excited state manifolds; they were estimated from values found for the Hg₂ system.²²

 $i = 0^+$, or 1_{ij}

The differential equations pertaining to the reaction scheme (2) were integrated numerically using a computer program which has been described elsewhere.²³ When the calculated total fluorescent intensity is plotted as a function of time after excitation, one would expect the resulting decay curve to contain 50 components, one for each vibrational level involved in the calculation. However, it was found that this curve could be quite accurately described by only two effective decay components; i.e., by a curve of the form $A_1 e^{-\kappa} 1^t + A_2 e^{-\kappa} 2^t$. The variations of κ_1 and κ_2 for both the 0_u^+ and 1_u states are shown in Figs. 6 and 7. This was found to be true for <u>both</u> the simulated 0_u^+ and 1_u decay schemes. It seems clear that the long decay component (Fig. 4) is

It seems clear that the long decay component (Fig. 4) is due to the fluorescent decay of the l_u manifold, because its lifetime is considerably longer than that found for other components (both measured and calculated). The variation of this component with pressure (Fig. 4) is followed qualitatively by the calculated curve (Fig. 7) and it can be thought of as arising from the change in the population distribution of l_u vibrational levels as a function of pressure and time after photoexcitation. The variation of the short component of the calculated l_u decay (Fig. 6) can be ascribed to a decrease in non-radiative lifetime with increase in pressure (Stern-Volmer behavior). Similar effects are apparent in the calculated fluorescent decay of the 0_n^+ state (Fig. 6).

The behavior of both the intermediate and short lifetimes found experimentally (Table II and Fig. 5) are rather more difficult to rationalize. It seems likely that the intermediate

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lifetime represents a <u>measured average</u> of the calculated short l_u and long 0_u^+ component (Fig. 6), the averaging being an artifact of the least squares fit. To illustrate this point we compare, in Fig. 8, the experimental decay curve obtained at 65 Torr (Fig. 8(a)), and the calculated 0_u^+ and l_u decay curves for $P_{Xe} = 65$ Torr (Fig. 8(b)). The calculated fluorescence decay from each manifold was summed, with equal weighting and adjusted to give the same peak height as the experimental curve. This was fitted to a <u>three</u> exponential decay, the resulting lifetimes being 157.7(5) ns, 4.78(1) ns, and 1.903(8) ns.

The short lifetime (Table II) is assigned to the short component of the calculated 0_u^+ decay (Fig. 6). The variation of the experimental short lifetime with pressure (Table II) is somewhat similar to that observed for both the intermediate and long lifetimes, although this measurement is subject to the most error because it lies near the limit of our timing capabilities (1.6 ns). The calculated short component of the 0_u^+ decay does not exhibit the marked increase in τ^{-1} at low pressures present in the experimental curve. This probably arises because of the relatively large Franck-Condon overlap between the vibrational levels at the top of the 0_u^+ and 1_u manifolds and the ground vibrational level of the 0_u^+ manifold.

Overall, the simple kinetic model used is in qualitative agreement with our measurements. However, our results at 5 and 120 Torr, which should approximate the radiative lifetimes of the upper and lower leves respectively, indicate that the radiative lifetimes calculated by Ermler, Lee, and Pitzer¹⁸ are somewhat too large. It should be noted, however, that Franck-Condon effects, which were not included by these authors, ¹⁸ may play a significant role.

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. Filtered Fluorescence Measurements

As a further test of the 0_u^+ and 1_u fluorescent decay model, lifetime measurements were also made with broad-band interference filters in the fluorescence channel. These were chosen to emphasize fluorescence from the first and the second continuum. The decay curves obtained were again fitted to three components.

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At pressures lower than 125 Torr the $\tau_{l_u}^{-1}$ versus P_{Xe} curves obtained with and without a filter in the fluorescence channel, tend to diverge (Fig. 4). This illustrates the deviation from a high pressure limit where fluorescence from only the lowest levels of the 0_u^+ and l_u manifolds are observed, because the filters effectively weight fluorescent decay from vibrational levels centered around their peak transmission. Some fluorescence from the lower levels is observed (at <u>ca</u>. 1700Å) with the 1325Å filter because the tail of its transmission function extends into the second continuum region.

Similar effects occur in the variation of intermediate reciprocal lifetime with pressure (Fig. 5), although because of the nature of this component the dispersion of the curves pertaining to measurements obtained with and without filters is expected to be more complex.

IV. SUMMARY

In conclusion, we have removed some confusion regarding the decay dynamics of the 0_u^+ and 1_u states of Xe₂, and have made a consistent analysis of their fluorescent decay. To achieve this, an excitation wavelength > 2kT below the ${}^{3}P_{2}-{}^{1}S_{0}$ absorption line was employed, thus avoiding formation of $Xe_2(0_u^+, 1_u)$ by three-body collisions. The study was strengthened by utilizing both a monochromator and interference filters in the fluorescence channel. By utilizing the theoretical life-time calculations¹⁸ we were able to qualitatively model the fluorescent decay of the 0_u^+ and 1_u states of Xe_2 . The decay dynamics can be summarized as follows.

(1) At $P_{Xe} \ge 100$ Torr, the 0_u^+ and 1_u states, populated in their upper vibrational levels, decay rapidly and only the lower level of each manifold fluoresces.

(2) At $P_{Xe} \leq 100$ Torr the relaxation data of others¹¹ were interpreted previously simply on the basis of a twostate (1st and 2nd continuum) model; however, a detailed study of the fluorescent lifetimes indicates that the true situation is too complex for this model to be valid. Intermediate vibrational levels of the 0⁺_u and 1⁻_u states participate in the kinetic scheme, giving rise to a measured three-component total fluorescent decay. All components exhibit a <u>decrease</u> in lifetime at $P_{Xe} \leq 20$ Torr and each can be assigned to the composite decay of vibrational levels of the 0⁺_u and 1⁻_u manifolds.

At very low pressures we expect, of course, to observe just the radiative decay of those vibronic levels which were populated by photoexcitation.

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A more complete study, using a high degree of monochromatization in the fluorescence channel, is clearly required in order to elucidate further the decay dynamics of this system and improve on the model proposed. When much higher intensity pulsed synchrotron radiation sources become available, such a study may be feasible.

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(e.s.d.	's in parentheses)			2	
$\tau_{0_u^+(high v)}^{(ns)}$	$\tau_0^+(\text{low v})$ (ns).	τ _{lu} (ns)	τ (ns) ^a	Reference	
	5.5(10)	96.5(50)		2	
			50(20)	3	
			130(20)	4	
		· ·	2000(500)	5	
	4(1)	16(2.5)		6 ^b	
			16(2)	7	
2		60		12	
	•	102(2)		9	
	6.0	770		14 ^C	
	• •	•	•	•	

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Compilation of lifetime measurements of lasing manifolds of Xe, Table I.

Unspecified. · a)

Observed 280ns decay and assigned it to a lifetime of a highly excited state. 6)

At 50 Torr. c)

Table II. Experimental values of $\tau_0^+, \tau_0^+, \tau_1^+, \tau_$

Pressure _{Xe}	(e ^τ 0 ⁺ (ns)			$\tau_0^+_u, \iota_u$ (ns)			τ _{lu} (ns)		
(Torr)	no filter	1325Å filter	1710Å filter	no filter	1325Å filter	1710Å filter	no filter	1325Å filter	1710Å filter
5	1.73(2)			7.4(4)		6.4(8)	53.2(7)		75.2(2)
11	1.96(3)	1.44(5)	1.51(5)	13.6(5)		8.6(6)	61.5(8)		75.(1)
25	2.57(2)	1.86(1)	2.02(6)	17.0(2)		18.5(6)	120.11(8)		103.(1)
65	2.64(3)	2.21(3)	3.1(2)	8.3(2)	5.9(3)	10.9(7)	105.3(3)	78.2(9)	83.1(4)
125	2.15(11)	2.38(6)		6.7(2)	6.2(6)		107.5(2)	108.(1)	102.(1)

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REFERENCES

- 1. C. K. Rhodes, IEEE J. Quant. Electron 10, 153 (1974).
- J. W. Keto, R. E. Gleason, Jr., and G. K. Walters, Phys. Rev. Lett. 33, 1365 (1974).
- 3. A. W. Johnson and J. B. Gerardo, J. Chem. Phys. <u>59</u>, 1738 (1973).
- S. C. Wallace, R. T. Hodgson, and R. W. Dreyfus, Appl. Phys. Lett. 23, 22 (1973).
- 5. R. Bouciqué and P. Mortier, J. Phys. D3, 1905 (1970).
- H. A. Koehler, L. J. Ferderber, D. L. Redhead, and P. J. Ebert, Phys. Rev. A9, 768 (1974).
- D. J. Bradley, M.H.R. Hutchinson, and H. Koester, Opt. Commun. 7, 187 (1973).
- 8. P. K. Leichner, K. F. Palmer, J. D. Cook, and M. Thieneman, Phys. Rev. <u>A13</u>, 1787 (1976).
- 9. P. Millet, A. Birot, H. Brunet, J. Galy, B. Pons-Germain, and J. L. Teyssier, J. Chem. Phys. <u>69</u>, 92 (1978).
- 10. E. H. Fink and F. J. Comes, Chem. Phys. Lett. <u>30</u>, 267 (1975).
- 11. R. Brodmann and G. Zimmerer, J. Phys. B 10, 3395 (1977).
- 12. M. Ghelfenstein, R. Lopez-Delgado, and H. Szwarc, Chem. Phys. Lett. 49, 312 (1977).
- M. Ghelfenstein, H. Szwarc, and R. Lopez-Delgado, Chem. Phys. Lett. 52, 236 (1977).
- 14. O. Dutuit, R. A. Gutchek, and J. LeCalvé, Chem. Phys. Lett. <u>58</u>, 66 (1978). (We thank R. A. Gutchek for communicating a manuscript of the above prior to publication.)

- -19-
- 15. For details see: E. Matthias, R. A. Rosenberg, E. D. Poliakoff, M. G. White, S.-T. Lee, and D. A. Shirley, Chem. Phys. Lett. <u>52</u>, 239,(1977).
- 16. It is a pleasure to acknowledge Dr. Victor Rehn who designed the focusing mirror.
- 17. J. W. Keto, R. E. Gleason, Jr., T. D. Bonfield, G. K. Walters, and F. K. Soley, Chem. Phys. Lett. 42, 125 (1976).
- 18. W. C. Ermler, Y. S. Lee, K. S. Pitzer, and N. W. Winter, J. Chem. Phys. <u>69</u>, 976 (1978).
- 18. (a) R. S. Mulliken, J. Chem. Phys. 52, 5170 (1970).
- 19. Calculations by Dutuit (personal communication) suggest that a small contribution to fluorescence at 1690Å may arise from radiative decay of upper 0_u^+ vibrational levels.
- 20. H. Bateman, Proc. Cambridge Phil. Soc. 15, 423 (1910).
- 21. T. D. Bonfield, F.H.K. Rambow, G. K. Walters, M. V. McCusker, D. C. Lorents, and R. A. Gutchek, Stanford Synchrotron Radiation Laboratory Users Group Meeting, 1978 (SSRL Report No. 78/09), Stanford University, Stanford, CA 94305.
- 22. M. Stock, E. W. Smith, R. E. Drullinger, and M. M. Hessel, J. Chem. Phys. 68, 4167 (1978).
- 23. G. Z. Whitten, "Rate Constant Evaluations Using a New Computer Modeling Scheme", paper presented at the 167th National Meeting of the American Chemical Society, Spring 1974.

FIGURE CAPTIONS

Figure 1. (a) Potential curves for the relevant electronic levels in Xe₂ after Fink and Comes.¹⁰

(b) Fluorescence spectrum of Xe₂.

- Figure 2. Schematic diagram of the monochromatized fluorescence apparatus.
- Figure 3. Decay curves following excitation of Xe_2 at 1508Å; (a) in the first continuum; (b) and (c) in the second continuum. In (c) the time scale is expanded to show the 0_u^+ lifetime.
- Figure 4. $10^3 \times \tau_{l_u}^{-1}$ (ns⁻¹) versus P_{Xe} (Torr), with values of τ_{l_u} taken from Table II. (The lines connecting the data points were included for clarity.)
- Figure 5. $10^2 \times \tau_{0_u^+, 1_u}$ (ns⁻¹) versus P_{Xe} (Torr), with values of $\tau_{0_u^+, 1_u}$ taken from Table II.
- Figure 6. Calculated fluorescent decay of the 0_u^+ manifold both short and long, and the short component of the $1_u^$ manifold as a function of Xe pressure.
- Figure 7. Calculated fluorescent decay of the long component of the l_u manifold as a function of Xe pressure.
- Figure 8. Experimental decay curve obtained at 65 Torr (a), and calculated decay of the 0_u^+ and 1_u manifolds at $P_{Xe} = 65$ Torr (b). The calculated curve was scaled to give the same peak height as the experimental curve.



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Fig. 1



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Fig. 2



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Fig. 3

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Fig. 4





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Fig. 3

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